

Examining Cases of Environmental Contamination Potentially Attributed to Unconventional Oil and Gas Extraction

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Advancements in unconventional drilling techniques, such as hydraulic fracturing and shale acidization, have made the extraction of natural gas and oil from previously inaccessible deep shale formations both practical and economically advantageous. Hydraulic fracturing involves a highly pressurized injection of water, proppants, and chemical additives to expand fractures in the shale formation to release trapped hydrocarbons. Despite the effectiveness of this technology to liberate previously sequestered natural gas and oil, it is not without environmental risk. Concerns over environmental stewardship have provided the impetus for multiple investigations designed to characterize the relationship between unconventional drilling and environmental quality.

At the forefront of the unconventional drilling debate are concerns over the potential migration of methane gas^{1, 2}, the leaching of harmful chemical compounds^{3, 4} and metal ions⁵, and the mishandling of produced and flowback waste water^{6, 7}, each of which can have a deleterious effect on groundwater reserves. There is also a growing concern over the relationship between unconventional drilling practices and regional air quality. Very limited air quality research has been performed; however, early data attribute rogue hydrocarbon emissions to unconventional drilling and hydrocarbon processing⁸. Preliminary findings have also identified gas flaring stations are sources of volatile organic carbons (VOCs) in surrounding air and soil (Hildenbrand et al., *unpublished*¹). However, it remains to be determined whether these emissions and the improper management of drilling waste fluids are accumulating in native plants and animals, ultimately entering into the human food chain and resulting in *ex situ* exposure.

When cases of potential contamination are called into question, extensive analytical measurements can be collected to differentiate between naturally occurring environmental changes and those attributed to anthropogenic activities. In the case of southern Parker County, Texas, the groundwater quality was called into question in 2010 as the result of the water coming from a private water well being visibly effervescent and having a petrochemical odor. The well owner discovered that his water could ignite and sustain a flame for a prolonged period of time, indicative of having elevated levels of dissolved flammable gases. In response to the concern over potential contamination from a nearby gas well, state and federal agencies began testing the water in this region for the presence of dissolved gases (methane, ethane, and propane), as well as for drilling-related chemical constituents used during gas well stimulation. The Texas Railroad Commission (TRRC) discovered high levels of benzene and explosive levels of dissolved methane, above their respective drinking water standards. The TRRC attributed the elevated methane levels to contamination from an intermediate gas layer known as the Strawn and deemed the water safe to

drink if the water was properly vented and aerated. This decision seemingly ignored the elevated levels of the carcinogenic benzene present above the 5 µg/L Maximum Contaminant Limit (MCL).

Further work was performed by the United States Environmental Protection Agency (US EPA). It was determined that the dissolved gas found in regional groundwater was a compositional and isotopic match to the gas being extracted from the nearby gas well from the Barnett shale layer. These results are the equivalent to a fingerprint match, in which the signatures of the two gases had the same ratios of methane/ethane and methane/propane, but also very similar ratios of carbon atom isotopes. The isotope ratio measurement techniques that were used are generally very precise and detailed. Data produced from highly specialized isotope ratio instrumentation are considered extremely reliable in environmental sourcing applications.

Since the initial observations of flammable water in 2010, Duke University, Stanford University, and The Ohio State University collaborated on a research study of the area, studying a handful of water wells in the area of concern. This study identified a number of mechanisms through which unconventional shale exploration could negatively affect surrounding groundwater⁹. It was determined that the rogue gas could be the result of a casing failure from one of the nearby gas wells. Alternatively, the contamination may be the result of interconnectivity between the shale layer and the overlying aquifer through geological fault lines that exist in southern Parker County. It was hypothesized that this could have been further accentuated through mechanical disruption caused during the well stimulation process⁹.

The Collaborative Laboratories for Environmental Analysis and Remediation (CLEAR) at The University of Texas at Arlington has also studied this region, as part of a collective effort to characterize groundwater quality in 550 wells from the Barnett shale region³. Of the notable findings from the southern Parker County region was one well that exhibited a dissolved methane concentration of 57.3 mg/L, more than twice the threshold of 28 mg/L, and above which the Department of the Interior and the Office of Surface Mining advises well owners to contact their local health authorities¹⁰. This sample also exhibited high levels of ethane and propane, characteristic of thermogenic natural gas that was created from buried organic material under high pressure. Isotopic analysis of the dissolved gases was also performed by The University of Texas at Austin to determine the origin of the gas.

In this study, a number of volatile organic carbon species were also detected in the southern Parker County area³. These included ethanol, methanol, propargyl alcohol, dichloromethane, cyclohexane, benzene, ethylbenzene, and xylene isomers. Benzene, ethylbenzene, and xylene are members of the BTEX family of compounds that are commonly used in unconventional energy extraction. Of particular concern, was the detection of dichloromethane and benzene, which were measured to be present at concentrations above their respective drinking water standards of 5 µg/L, as suggested by the US EPA's Safe Drinking Water Act. Subsequent analyses on select wells in the area have revealed methane concentrations as high as 66 mg/L, in addition to an increased penetrance of natural gas constituents: hexane, cyclohexane, methylcyclohexane, dimethylcyclopentane, octane, heptane, and pentane. Additional mobile mass spectrometry measurements have also detected BTEX and naphthalene derivatives and spectrophotometric measurements that have revealed methane and propane concentrations of 155,000 and 32,000 parts-per-million (ppm), respectively. These values are above the lower explosive limits for both of these gases (50,000 ppm for methane and 21,000 ppm for propane). Overall, fluctuations in the concentrations and the detections of these compounds indicate that the groundwater quality in this region is highly variable, warranting the extensive time-series analysis that is currently ongoing in southern Parker County (Hildenbrand et al., *unpublished*²).

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